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Rapid Solid-State Metathesis Routes to Aluminum Nitride

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Metathesis (exchange) reactions offer the possibility of controlling temperature through a judicious choice of precursors. Here, a reaction between $AlCl_3$ and Ca_3N_2 is found to produce phase-pure aluminum nitride (AlN) in seconds. The $CaCl_2$ byproduct salt, whose formation drives this highly exothermic reaction, is simply washed away after reaction completion. SEM images demonstrate that the AlN product is a micron-sized powder, while TEM shows well-formed crystallites. Thermodynamic calculations indicate that a reaction temperature of 2208 K could be reached under adiabatic conditions. Using an in situ thermocouple and a stainless steel reactor vessel to hold the precursors, a reaction temperature of 1673 K is measured 0.8 s after initiation. Switching to a thermally insulating ceramic vessel produces a maximum reaction temperature of 2010 K because of the more nearly adiabatic conditions. The high reaction temperature appears to be critical to forming phase-pure AlN. Experiments with Li_3N, instead of Ca_3N_2, produce lower temperatures (1513 K), resulting in both Al and Al_2O_3 impurities.

Introduction

Miniaturization of high-power electronic devices greatly increases the amount of thermal energy produced per unit area during their operation. This creates a need for materials that can dissipate heat rapidly to avoid electronic or mechanical failure.[1] Aluminum nitride (AlN) is an important thermal management material for silicon-based electronics because of its low coefficient of thermal expansion (4.3×10^{-6} K^{-1}), closely matching that of silicon, and its very high thermal conductivity (320 W m^{-1} K^{-1}).[2] AlN is an insulator with a large band gap ($E_g = 6.4$ eV), high resistivity ($>10^{11}$ Ω m), and low dielectric constant (8.6).[3] These physical properties make AlN promising for use as an electronic substrate and as a packaging material for circuits.[4] Other applications for AlN include UV photodetectors, pressure sensors, thermal radiation sensors, and field-effect transistors.[5,6]

There is a need for new synthetic approaches to AlN and other nitrides, because most current methods are time-consuming and/or expensive. Syntheses of AlN often involve processes with complex equipment, such as ion beam evaporation[4] or DC arc plasma, which forces aluminum ingots to react with ammonia or nitrogen gas under extreme conditions.[7] Another synthetic method, carbothermal reduction, involves the conversion of Al_2O_3 and C in a N_2 or NH_3 atmosphere into AlN at high temperatures (>1600 K) for several hours.[8] Self-propagating high-temperature synthesis represents an additional route to AlN, in which Al metal powder is reacted with elemental nitrogen or NaN_3 at high pressures (>1000 atm) and temperatures (up to 1900 K).[9] One drawback to this synthesis is incomplete nitridation, especially at lower pressures. A major challenge is to obtain a high yield of pure AlN at moderate temperatures and low pressures.

Solid-state metathesis (exchange) reactions offer the advantages of a rapid, high-yield method that starts from room-temperature solids and needs little equipment. The idea behind metathesis reactions is to use the exothermicity of

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salt formation to rapidly create a desired product. A metal halide is combined with an alkali or alkaline earth main-group compound to produce the desired product plus a salt that is then washed away with water or alcohol. Metathesis reactions have proven to be successful in the synthesis of a number of crystalline refractory materials including borides,[10] chalcogenides,[11,12] and nitrides.[13−15]

Once initiated, metathesis reactions reach high temperatures (>1200 K) in a fraction of a second and cool very quickly (often <5 s). Because of the rapid nature of these reactions, nucleation and growth are quickly terminated, generally resulting in small crystallites and occasionally forming metastable phases.[11,16] Previous attempts to make AlN via metathesis reactions resulted in oxide impurities.[17] Here, phase-pure AlN is synthesized in seconds from a metathesis reaction between Ca_3N_2 and $AlCl_3$. The use of Ca_3N_2, which increases the temperature of the reaction, is critical to avoiding impurities. Products are characterized using powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and in situ temperature analysis.

Experimental Section

The precursors $AlCl_3$ (Strem, 99.99%), Al_2S_3 (Cerac, 99.9%), Li_3N (Cerac, 99.5%), and Ca_3N_2 (Cerac, 99%) were used as received. AlI_3 was formed by heating its constituent elements (Al, Cerac, 99.5%; I_2, Fisher) through a vapor-transport reaction in an evacuated, sealed Pyrex tube using a temperature gradient from 463 to 623 K, as modified slightly from a literature preparation of GaI_3.[18]

The synthesis of aluminum nitride was carried out in a helium-filled glovebox (Vacuum Atmospheres MO-40). The amounts of reactants were adjusted to produce 0.20 g (4.8 mmol) of AlN product. Stoichiometric amounts of the reactants were weighed and ground together with an agate mortar and pestle. The reactants were then transferred to a stainless steel (or ceramic) cup and placed within a larger capped steel reaction vessel, modeled after a bomb calorimeter.[19] This allows for containment of any gases produced. The reaction is initiated through the use of a resistively heated Nichrome wire and is complete in less than a second. *Warning:* Solid-state metathesis reactions are highly exothermic and can initiate as the reagents are being ground together. Precautions should be taken before performing this type of reaction, and extreme care should be used when scaling up reactions. The reaction products are then removed from the drybox and washed in 0.5 M HCl or 1.0 M H_3PO_4. While the aqueous washing solution removes the byproduct salt, the acid prevents base-catalyzed hydrolysis of the product.[20,21] To reduce the amount of time the AlN is in the aqueous solvent, the product is immediately vacuum filtered and then dried in a furnace at 450 K. Because cellulose filter paper cannot withstand the acid washing, glass microfiber filter paper (Millipore) is used instead.

In situ reaction temperature measurements were made by modifying the stainless steel reactor. A hole was drilled through the bottom of both the steel canister and the reaction cup. A thermocouple was threaded through the hole and placed directly into the reaction mixture and secured with ceramic paste. A computer was connected to the thermocouple and programmed to record one data point every millisecond.

Product Characterization

Powder X-ray diffraction was performed on the washed products using a Crystal Logic $\theta-2\theta$ diffractometer with a graphite monochromator and Cu $K\alpha = 1.5418$ Å radiation. The scans were taken between 10 and 100° 2θ at 0.1° intervals with a 3-s count time. Least-squares refinement was carried out using MacDiff (http://www.geol.uni-erlangen.de/html/software/Macdiff.html) to fit the X-ray diffraction peaks and Unit Cell (http://www.esc.cam.ac.uk/astaff/holland/UnitCell.html) to then calculate the lattice parameters. In situ reaction temperatures were measured in a modified reactor with 0.03-in.-diameter C-type (Omega, 26% rhenium/84% tungsten versus 5% rhenium/85% tungsten) high-temperature thermocouples, which were placed directly into the reaction mixture. Scanning electron microscopy (SEM-Stereoscan 250) was used to characterize surface structure and particle size of the product. Transmission electron microscopy (TEM JEOL 100CX) provides a fuller picture of the morphology of the AlN crystallites. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Pyris Diamond TG/DTA, from room temperature to 1770 K, at increments of 10 °C/min.

Results and Discussion

Solid-state metathesis reactions between the aluminum precursors ($AlCl_3$ or Al_2S_3) and the nitriding agents (Li_3N or Ca_3N_2) proceed in a rapid, exothermic manner upon initiation with a resistively heated Nichrome wire, as follows

$$AlCl_3 + Li_3N \rightarrow AlN + 3LiCl \tag{1}$$

$$0.5Al_2S_3 + Li_3N \rightarrow AlN + 1.5Li_2S \tag{2}$$

$$AlCl_3 + 0.5Ca_3N_2 \rightarrow AlN + 1.5CaCl_2 \tag{3}$$

The real driving force behind each reaction is the formation of an ionic salt ($LiCl$, Li_2S, or $CaCl_2$), which is so favorable that the reactions become self-propagating. The salt that is produced can then be washed away.

When choosing reagents for metathesis reactions, several important factors must be considered, including the stability of products versus reactants, the temperatures at which the precursors change phase, and the maximum reaction temperature. Clearly, the products must be considerably more stable than the reactants to create an exothermic reaction that will self-propagate. A phase change of one of the precursors is generally needed to initiate a solid-state metathesis

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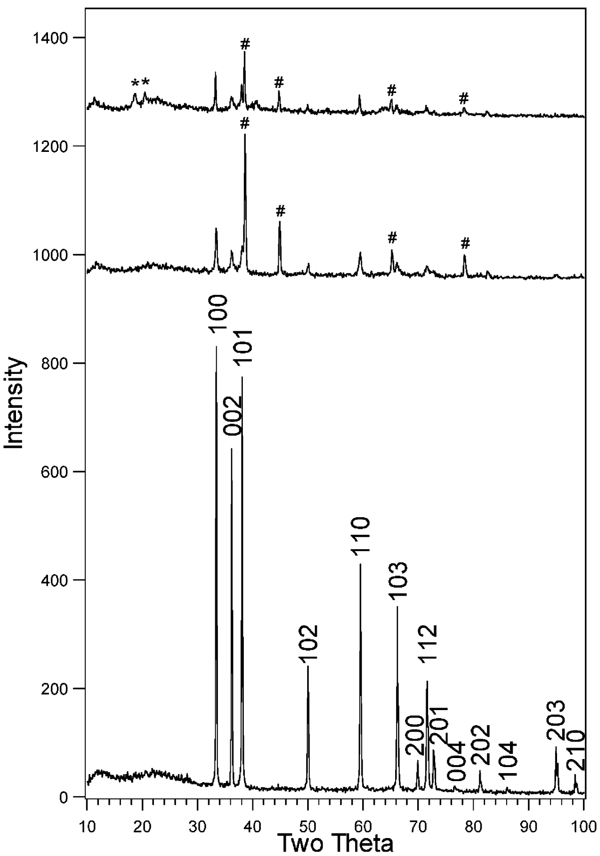

Figure 1. Powder X-ray diffraction patterns of the washed products from the following solid-state metathesis reactions that produce AlN: $AlCl_3 + Li_3N$ (top), $0.5\ Al_2S_3 + Li_3N$ (middle), and $AlCl_3 + 0.5\ Ca_3N_2$ (bottom). The Miller indices (*hkl*) for hexagonal AlN are given in the highly crystalline pattern produced by reacting $AlCl_3$ with Ca_3N_2 (bottom). Aluminum (#) and alumina (*) impurities are found in the other reactions.

reaction.[22] Once initiated, the heat generated by salt formation needs to be sufficient to keep the salt produced in a molten state. If this is the case, the reaction will be self-propagating.[10] Theoretical reaction temperatures can be calculated using the enthalpy of reaction (ΔH_{rxn}), temperature-dependent heat capacities (C_p), and enthalpies of phase changes. The adiabatic maximum reaction temperatures, referred to as T_{max}, assume that reactions proceed to completion with no heat loss.

The synthesis of AlN was approached by considering several possible precursors, including aluminum halides or chalcogenides in combination with alkali or alkaline earth nitrides. Figure 1 shows a progression of products from a low-quality nitride contaminated with both aluminum metal and aluminum oxides to a phase-pure, high-quality nitride.

The metal chloride ($AlCl_3$) was chosen first because of its relatively low cost and low sublimation temperature (453 K). $AlCl_3$ was ground together with Li_3N, the mixture was placed in a stainless steel reactor, and the reaction was initiated with a Nichrome wire (eq 1). This reaction produces moderately crystalline AlN (Figure 1, top); however, there is contamination from Al metal and alumina. The aluminum impurity most likely results from reduction of the $AlCl_3$ precursor during reaction. Alumina, on the other hand, likely forms as a result of the aqueous wash, either from unreacted precursors or from hydrolysis of small, poorly formed AlN particles that are more susceptible to oxidation. Note that alumina is not observed in powder X-ray diffraction patterns taken before washing, but Al metal is.

Changing the precursor from $AlCl_3$ to AlI_3 results in products and impurities similar to those found with $AlCl_3$. Because the melting point of AlI_3 is 461 K—versus 453 K for the sublimation temperature of $AlCl_3$—the reaction initiates at nearly the same temperature. A comparable T_{max} is observed, along with aluminum and alumina impurities.

To achieve greater nitridation of the product, Al_2S_3 was substituted for $AlCl_3$. The idea is that, because Al_2S_3 has an anion with a doubly negative charge, a more stable byproduct salt, Li_2S, is expected. The ΔH_f for Li_2S is -446.9 kJ/mol, compared to a ΔH_f of -408.4 kJ/mol for LiCl.[23] Aluminum sulfide was mixed and ground together with Li_3N in an agate mortar and pestle, the mixture was placed in the stainless steel reactor, and the reaction was initiated with a heated filament. The products were then removed from the He atmosphere drybox, filtered, and dried in an oven at 450 K (Figure 1, middle). The AlN produced from the reaction of Al_2S_3 and Li_3N is slightly more crystalline than that formed from $AlCl_3$ and Li_3N (Figure 1, top), and the Al_2O_3 impurity is eliminated. However, unwanted Al metal still presents a problem.

The persistence of metallic Al in the product at first suggested that more nitriding agent might be needed. Thus, several nitrogen-containing salts including NH_4Cl, NaN_3, and $LiNH_2$ were added into the reactions. As the reactions release heat after initiation, these salts decompose, and can supply either nitrogen or ammonia to aid in nitride formation.[14,24] However, instead of increasing the crystallinity of the nitride product, all of these additives resulted in less-crystalline products with more impurities. Adding an excess of nitride starting material also yielded only negative results. The commonality among these attempts to improve the reactions is that excess reagents act as heat sinks and lower reaction temperatures. Because this leads to less-crystalline products, a method was sought that would instead raise the reaction temperature. Aside from the possibility that AlN might simply form more readily at elevated temperatures, higher temperatures have other advantages, including more energy available to surmount activation barriers and an increased probability of reactants finding each other in the short time of reaction. Additionally, once the product forms, crystal growth will continue as long as the byproduct salt remains molten due to Ostwald ripening.[25,26] Because hotter reactions take longer to cool, more time will be available for crystal growth, generally leading to higher crystallinity along with greater yields.

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Table 1. Calculated and Measured Reaction Temperatures of AlN-Producing Solid-State Metathesis Reactions

reaction	$T_{\mathrm{max,calc}}$ (K)	$T_{\mathrm{max,exp}}$ (K)	$T_{\mathrm{max,salt}}$ (K)
$AlCl_3 + 0.5Ca_3N_2 \rightarrow AlN + 1.5CaCl_2$	2208	1673 (2010)[a]	1427
$AlCl_3 + Li_3N \rightarrow AlN + 3LiCl$	1656	1513	1503
$0.5Al_2S_3 + Li_3N \rightarrow AlN + 1.5Li_2S$	2073	1373	1086

[a] Reaction carried out in insulated ceramic reactor.

Using Al_2S_3 but changing the nitriding agent to Ca_3N_2 was expected to achieve a higher reaction temperature with the possibility of producing AlN with enhanced crystallinity because the calcium sulfide byproduct salt is very stable ($\Delta H_f = -473.2$ kJ/mol). Unfortunately, the reaction of Ca_3N_2 and Al_2S_3 did not propagate. This is likely related to the very high melting point of the byproduct salt CaS (mp = 2524 K). Previous experiments have shown that, if the energy generated by salt formation only is insufficient to keep the salt produced in a molten state, propagation will cease. This value, called $T_{\mathrm{max,salt}}$, was calculated for each reaction and presented in Table 1. For the reaction between Al_2S_3 and Ca_3N_2, $T_{\mathrm{max,salt}}$ is 1202 K, well below the melting point of CaS, and therefore, it is not surprising that this reaction does not self-propagate.

The aluminum precursor was therefore changed back to $AlCl_3$ while maintaining Ca_3N_2 as the nitriding agent. The maximum adiabatic temperature predicted for the reaction of Ca_3N_2 and $AlCl_3$ is 2208 K—over 550 K above the value calculated for the reaction between Li_3N and $AlCl_3$. This predicted increase in reaction temperature is mainly due to the higher thermodynamic stability of the byproduct salt $CaCl_2$ ($\Delta H_f = -795$ kJ/mol) versus LiCl ($\Delta H_f = -408.4$ kJ/mol).[23] Because the value for $T_{\mathrm{max,salt}}$ (1427 K) is now above the melting point of the $CaCl_2$ salt byproduct (1045 K), this reaction is expected to propagate. As hoped, this reaction not only propagates rapidly but succeeds in producing single-phase, crystalline hexagonal AlN (Figure 1, bottom). A least-squares refinement of the X-ray data gives lattice parameters of $a = 3.1090$ Å and $c = 4.9749$ Å ($\pm$0.0012 Å), which closely matches the literature values of $a = 3.1114$ Å and $c = 4.9792$ Å (JCPDS no. 25-1133). The Al content of the AlN is 48 mol % (50% expected) based on thermogravimetric analysis carried out in air to 1773 K, which converts all of the AlN to Al_2O_3 (corundum). The slightly lower than expected Al content might be due to some surface phosphate left from the acid wash. The yield of the product is typically about 80%, based on a reaction scale of 0.2 g. A larger reaction scale is likely to increase the yield significantly.[27] At the 0.2-g reaction scale, mechanical losses of product due to transfers and material trapped in the filter paper is significant. The relative amount of these losses would be less important at larger scales. However, caution is advised in scaling up these highly exothermic reactions.

To measure the actual temperatures achieved in the AlN-forming reactions, type C thermocouples were inserted directly into the stainless steel reaction vessels. Temperature profiles for each reaction are presented in Figure 2. As expected, the least energetic reaction, $Al_2S_3 + Li_3N$ (Figure 2d), produced the lowest $T_{\max}$ (1373 K). The reaction of $AlCl_3$ with Li_3N increased the measured $T_{\max}$ to 1513 K (Figure 2c). Switching from Li_3N to Ca_3N_2 resulted in a further increase in $T_{\max}$ to 1673 K, which was reached 0.8 s after initiation of the reaction (Figure 2b).

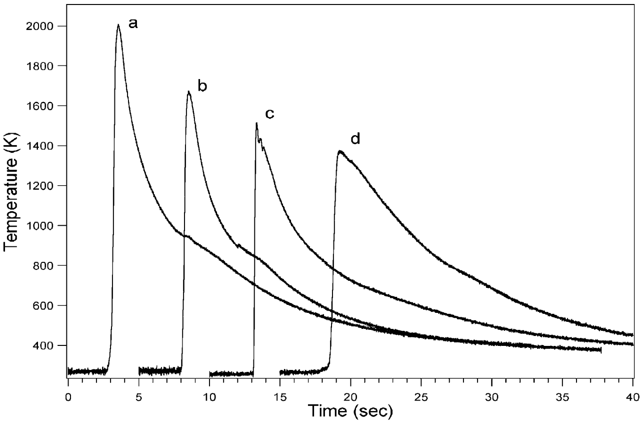

Figure 2. In situ temperature measurements for the following AlN reactions: (a) $AlCl_3 + 0.5\ Ca_3N_2$ in an insulating cup, (b) $AlCl_3 + 0.5\ Ca_3N_2$, (c) $AlCl_3 + Li_3N$, and (d) $0.5\ Al_2S_3 + Li_3N$.

Although the reaction with calcium nitride reached higher temperatures than the reactions with Li_3N, as expected from the $T_{\max}$ calculations (see Table 1), it is apparent that the measured temperatures are considerably lower than the calculated theoretical maximum temperatures. This is most likely due to nonadiabatic conditions. The high thermal conductivity of the stainless steel reaction vessel suggested that this might be largely responsible. Thus, in the hope of improving the experimental $T_{\max}$ value, the reaction of $AlCl_3 + Ca_3N_2$ was repeated in a thermally insulating ceramic cup. The result was an increase of over 300 K in $T_{\max}$ to 2010 K. This result is much closer to the calculated adiabatic value of 2208 K. Additionally, an increase in the crystallinity of the product was observed (Figure 1, bottom). Because slower heat dissipation results in the product remaining in the molten salt matrix for longer times, more Ostwald ripening, and hence enhanced crystallinity, occurs. This, in turn, makes the AlN product more resistant to hydrolysis in water.

From the in situ temperature measurements, it appears that $T_{\max} \geq 1673$ K is needed to produce phase-pure AlN via metathesis reactions. Either products formed in cooler reactions never attain enough heat to produce AlN or the low crystallinity of the AlN particles formed make them vulnerable to attack during the aqueous wash. These results explain why Ca_3N_2 is preferable to Li_3N as a nitriding agent for reactions with aluminum halides.

Thermal dissipation explains why the $T_{\max}$ results are lower than predicted for $AlCl_3 + Ca_3N_2$ and $AlCl_3 + Li_3N$, but does not entirely describe the case of Al_2S_3, where in situ measurements are found to be only about one-half of the calculated adiabatic values. Because the $T_{\mathrm{max,salt}}$ of this reaction is less than the melting point of Li_2S (the byproduct salt), this reaction was not expected to propagate. However, some AlN is produced through this reaction. To understand

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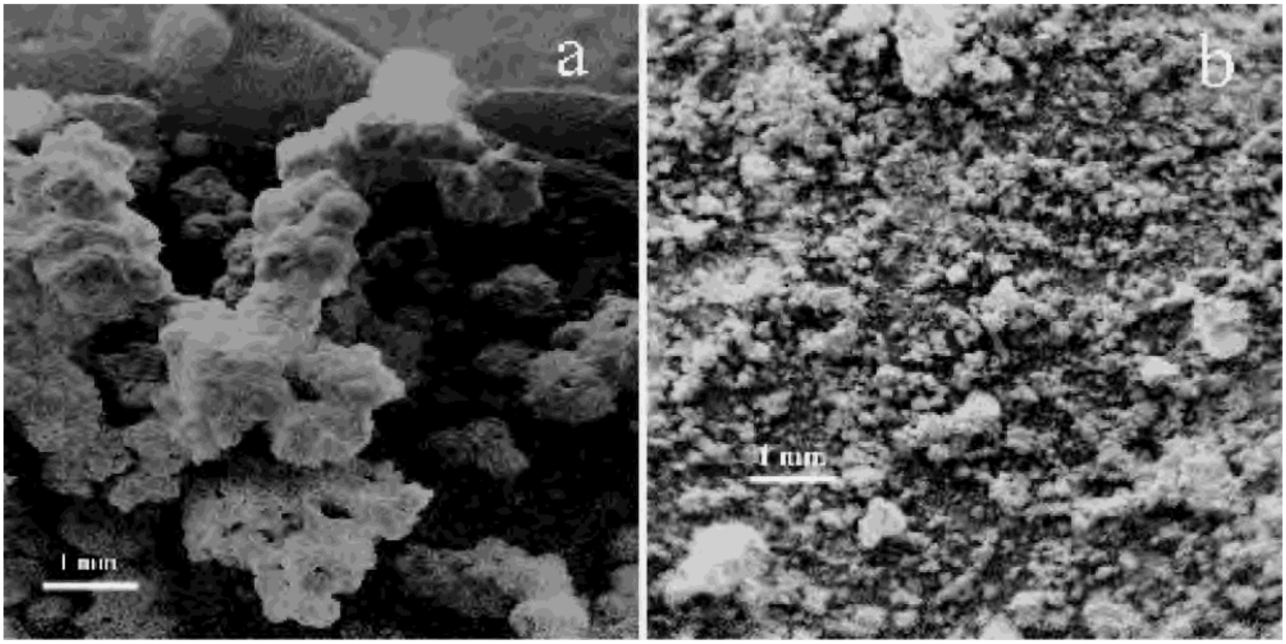

Figure 3. Scanning electron microscopy (SEM) images of the AlN product formed in the reaction between $AlCl_3$ and Ca_3N_2: (a) before acid washing, the product appears as a melt of $CaCl_2$, and (b) after acid washing, pure AlN appears as a fine micron-sized powder.

why this occurs, it is worth considering the temperatures at which the reactants change phase. $AlCl_3$ sublimes at approximately 453 K, whereas Al_2S_3 does not melt until 1645 K.[23,28] Because the Nichrome wire detonator heats to near 1100 K when current is run through it, there is ample energy to vaporize some of the molecular solid $AlCl_3$, but not the extended network structure of Al_2S_3, which remains in solid form. Thus, the stability of Al_2S_3 leads to an incomplete reaction with Li_3N, while the high melting point of Li_2S (the byproduct salt) prevents self-propagation because a molten salt does not form (the melting point for $Li_2S > T_{max,salt}$). This explains why the observed T_{max} value is much lower than expected.

The morphologies of the products were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). An SEM image of the $AlCl_3 + Ca_3N_2$ reaction product is shown before (Figure 3a) and after (Figure 3b) washing in acid. Figure 3a demonstrates that, before the byproduct $CaCl_2$ is washed away, the product appears as a molten salt ($CaCl_2$). After being washed in 1 M phosphoric acid to remove the $CaCl_2$ byproduct salt, the product appears as expected—a white, fluffy, micron-sized powder. The AlN product is composed of well-formed, micron-sized crystallites as imaged with TEM (Figure 4). The edges are well-defined, thus demonstrating that hydrolysis has not destroyed the surface morphology of the sample.

Conclusions

A solid-state metathesis reaction between $AlCl_3$ and Ca_3N_2 is shown to be a fast, reliable method for producing high-quality aluminum nitride. The driving force behind the reaction is the formation of a thermodynamically stable byproduct salt that is easily removed from the nitride product through an acid wash/filtration process. This highly exothermic reaction reaches a temperature above 2100 K within a fraction of a second and then quickly cools to room temperature. Theoretical maximum reaction temperature

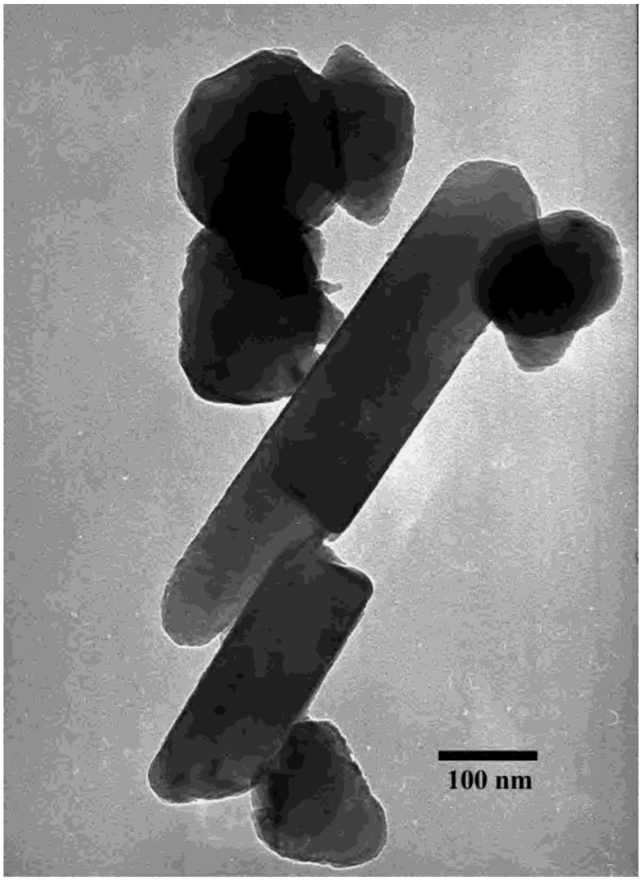

Figure 4. Transmission electron microscopy (TEM) image of representative AlN product demonstrating well-formed crystallites and micron-sized domains.

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calculations based on thermodynamic data and in situ temperature measurements were used to gain an understanding of these metathesis reactions. Higher sustained reaction temperatures are necessary for the formation of phase-pure AlN. At lower temperatures, incomplete nitridation leads to aluminum impurities as well as aluminum oxide, which forms upon washing. Extension of this method to produce other nitrides using Ca_3N_2 as the nitriding agent along with a thermally insulating ceramic reaction vessel is now in progress.

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